A method of preparation and some properties of a starch gel

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Much of the work on starch has been on saccharification and very little on the colloidal properties, particularly those of the starch gel. Although starch in the gel condition does not exist in nature, it is interesting both from a colloidal chemical standpoint and also in relation to carbohydrate gels such as agar or cellulose.

It is difficult to prepare a starch gel which is stiff enough to be handled without breaking and crumbling, and it is almost impossible to make good gels of very high concentration, such as the one used here, by the usual procedure. It was with this idea in view that the following method was used. A 100 grams of commercial corn starch were well mixed with 150 c.c. of cold distilled water, and the mixture then poured into covered petri dishes. Enough starch solution was poured into each dish so that the bottom was just covered. A number of these dishes were then put in the autoclave for thirty minutes at a temperature ranging from 105° to 110° C. When still warm the starch was cut into strips. They were then put over the radiator to dry, later in the oven at 35° C., and finally dried in a desiccator over calcium chloride to constant weight. The starch prepared in this manner does not break on handling and when placed in water, at low temperatures, is only very slightly soluble. When completely dry it is somewhat transparent and tough. The transparency disappears again after standing in water for twenty four hours, but even after this it ir still fairly tough. Strips of this starch were weighed, put in 100 c.c. of distilled water and left for twenty-four hours at different temperatures. Surface water was removed by dipping the strips quickly into alcohol and ether and blotting on filter paper. They were then weighed to determine the amount of water adsorbed. In all cases the starch kept its shape and at low temperatures was hard and firm.

The water in which the starch strips had been standing turned

blue with iodine, but the amount of starch dissolved at low temperatures was not large. This increases as the temperature rises. Strips of the starch gel were placed in 100 c.c. of water and allowed to stand for twenty-four hours. An aliquot portion of the liquid was taken, evaporated and dried to constant weight in a desiccator. TABLE I gives the results, taken from only one deter-

TABLE I

	Temperature degrees Centigrade			
	35	70	80	90
Dry weight of strip in grams	2.064	0.800	0.679	0.664
Volume of water remaining after adsorption, cc.	97.768	97.432	97.634	97.402
Starch residue in 25 cc. of above water, in grams	0.001	0.006	0.016	0.030
Total weight of starch residue, in grams	0.039	0.024	0.061	0.117
Per cent weight of original strip dissolved	0.19	2.90	9.06	17.60

mination in each case. In plotting the graph as indicated by the above figures it is apparent that there is a very sudden rise in the amount of the gel which passes into solution at 70° C. At the lower temperatures the correction would be negligible as is shown in TABLE II. The correction has been applied tentatively for the reason named above, since it would require more than one determination to determine it definitively. In any event it is obvious that the adsorption of water per gram starch gel would actually be even greater than as given in the tables at the end of this paper. It seems possible that the substance dissolved in the water does not do so immediately, but only on standing. No work, however, was done to determine this. The liquid at 90° C. and also those at lower temperatures gave no test for reducing sugars with Fehling's solution. At the higher temperatures the strips became larger and softer than at the lower but kept their shape.

A microscopical view of a section of one of these starch strips showed that it did not have a homogeneous structure but was made of partially decomposed starch grains with a jelly-like substance between them which cements or holds them together. These partly swollen grains appeared unchanged even after boiling ten minutes in water. There may have been a slight increase in size, but no measurements were taken to determine this. It is the opinion of the writer that the starch grains only

partly swelled, at the temperature at which the gel was made, due to lack of water. It will be remembered that the gel was highly concentrated, $66^2/_3$ per cent, and it may be that swelling goes on forming a paste and leaving the grains only slightly changed, due to the insufficient supply of water present. A 10 per cent gel made by mixing starch and cold water and adding boi ing water to it contains empty sacs in the gelatinous mass. A 2 per cent gel after boiling five minutes showed these empty envelopes. These are probably the individual covers of the starch grains. Whether further disintegration takes place in the grains of the gel used in this work on standing in water at higher temperatures is not known, but investigation will be carried on along this phase of the problem.

Meyer (**5**), in his work on starch, observed these sacs. The early stages in swelling correspond to those seen in the gel used here. In this formation, according to him, the swelling continues until the sac is formed. In the beginning striations appear which disappear when the sacs become larger. Later the walls of the sacs wrinkle and when swelling is complete the walls of these collapsed sacs consist of a gel which is made of amicroscopic drops. Meyer also worked with corn starch. He prepared it by first mixing the starch with cold, and then with boiling, water. When the vessel containing the starch was placed in boiling water for five minutes all the grains were swollen and the sacs floated freely in the sol. The partly swollen grains, observed by the writer, appeared much as Meyer has described them. The contents were striated, the stripes running out from the center, and in the weaker gels the sacs seemed empty.

The gel is fairly resistant to heat. When newly made and while still hot, if boiled in water for fifteen minutes, only a small part went into solution. If the gel is allowed to set entirely, the amount dissolving becomes less. Gels fully dehydrated when boiled fifteen minutes kept their shape. They dissolved somewhat, however, as the liquid gave the characteristic blue color with iodine. If a 10 per cent sol, when still hot, (i.e. immediately after making) is put into boiling water, it dissolves. When the same gel is set and then boiled fifteen minutes only part of it goes into solution. It would appear from this that the setting of the sol is what makes

it partly irreversible at the temperature of boiling water. The higher the concentration of the sol the quicker the setting takes place, so that the starch used in this work was practically set when removed from the autoclave. This agrees with examples given by Meyer (**5**), showing that the setting of a sol at a certain temperature is more rapid the higher the concentration.

Maquenne and Roux (**3**, **4**) found that ordinary starch paste contained 80–90 per cent amylocellulose and the rest amylopectin. This they concluded from the results of iodine and saccharifying tests. They considered the geling properties of starch were due to the amylopectin. The amylocellulose was partly soluble in boiling water and completely liquified, according to Roux (**6**), in excess of water at 150° C. and had no geling power. At 90° C. 18 per cent of the gel goes into solution, according to the work of the writer. It may be that this is all amylopectin of Maquenne.

Taylor (**7**, p. 127) mentions the fact that starch sols are like silicic acid sols in their behavior, but does not state in what manner. The gel, however, seems to simulate more closely the elastic gels of agar and gelatine than the rigid one of silicic acid. Even these elastic gels have to be heated to a higher temperature than that at which gelation occurred before they will again become sols. The geling and melting points, in the case of gelatine, however, vary with the concentration and are also affected by organic substances and salts.

The general averages of the determinations given in the tables at the end of this paper, under APPENDIX, are shown in TABLE II, below. In the work carried on by the writer, with the range of temperatures used, the higher the temperature the more water was absorbed. Thus it is evident from the following figures there was no maximum point above which the adsorption decreased, at least up to 90° C. For at 8.5–10.5° C. the average adsorption is 0.864 grams water per gram dry starch, whereas at 90° C. it has risen to 3.713 grams of water, an increase of over four times that at about 8° C. As the temperature was raised the size of the strips increased upon swelling; they became softer and of a less tough and firm consistency. In some of the solutions at high temperatures there were minute shiny particles, the nature of which was not determined.

TABLE II

GENERAL AVERAGES FROM TABLES III–XI (SEE APPENDIX)

Temperature degrees Centigrade	Adsorption water per gram dry starch gel on basis of original weight	Adsorption water per gram, corrected according to TABLE I
8.5–10.5	0.864	correction negligible
17.5	0.896	" "
24	0.916	" "
35	1.140	1.142
50	2.426	2.448
60	2.807	2.865
70	3.153	3,274
80	3.427	3.768
90	3.713	4.411

In MacDougal's work with artificial biocolloid mixtures (1), mainly of agar but containing some protein, an increase in the total amount of swelling was found to a maximum point between 39° and 46° C. MacDougal (2) has also shown a greater swelling of agar than of gelatine in distilled water at the same temperature, and in mixtures of the two the swelling increased as the percentage of agar in the mixture was increased. From these results, and also from those shown in this paper, it would appear that at least carbohydrate gels behave somewhat similarly.

This increased adsorption with rise in temperature does not agree with Taylor (7, p. 155), who states that, according to LaChatelier's theorem, heat diminishes and cold and pressure increase imbibition. But Meyer (5) refers to the fact that gels dried in the air will swell again if put into water, the swelling being greater the higher the temperature of the water. The temperatures at which the writer's experiments were performed varied slightly from that taken as the average, but in no case was it enough to be noticeable in the amounts of water adsorbed.

The preparation of this starch gel was undertaken with the idea of obtaining a pure carbohydrate gel, which on account of its hydrative capacity would be suitable for experimentation under various conditions. In a sense it might be said to simulate a cellulose membrane, but it would be unsafe to carry the comparison too far. Inasmuch as the hydration of organic elastic gels is of fundamental importance in many physiological problems which are attracting great attention today, it has seemed worth while to place on record the results of the above experiments as a contribution to a partial knowledge of some of the properties which

this starch gel presents. The study of such systems becomes of interest, not only on account of the mere increase in size—the swelling which takes place on immersion in water with the implications that such phenomena have as regards growth phenomena—but also on account of its possible relation to problems of metabolism.

Since no chemical analyses were made (except those for reducing sugars in the water in which the strips had stood), the writer cannot say whether any changes took place in the starch due to the temperatures employed, either in the structure of the starch grains or chemically, but simply gives this method as a means of preparing a fairly resistant starch gel which is easily handled.

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APPENDIX

TABLE III

WEIGHT OF WATER ADSORBED BY DRIED STARCH GEL IN GRAMS AT TEMPERATURE FROM 8.55 TO 10.5° C.

Original starch gel taken	After 24 hours in water	Gain	Water adsorbed per gram starch
1.320	2.552	1.232	0.933
1.073	1.937	0.864	0.805
1.107	2.045	0.938	0.847
1.552	2.821	1.269	0.817
1.484	2.743	1.259	0.848
0.932	1.709	0.777	0.833
0.970	1.809	0.839	0.864
1.067	1.984	0.917	0.859
0.741	1.462	0.721	0.973
0.897	1.667	0.770	0.858
			0.864

TABLE IV

WEIGHT OF WATER ADSORBED BY DRIED STARCH GEL IN GRAMS AT TEMPERATURE ABOUT 17.4° C.

Original starch gel taken	After 24 hours in water	Gain	Water adsorbed per gram starch
1.438	2.716	1.278	0.888
1.499	2.781	1.282	0.855
1.032	1.991	0.959	0.929
1.827	3.381	1.554	0.850
0.856	1.692	0.836	0.976
0.903	1.818	0.915	1.013
1.327	2.610	1.283	0.967
1.202	2.350	1.148	0.955
2.013	2.688	1.675	0.832
1.920	3.498	1.578	0.821
1.076	1.951	0.875	0.813
1.396	2.592	1.196	0.856
			0.896

TABLE V

WEIGHT OF WATER ADSORBED BY DRIED STARCH GEL IN GRAMS AT TEMPERATURE ABOUT 24° C.

Original starch gel taken	After 24 hours in water	Gain	Water adsorbed per gram starch
2.642	5.103	2.461	0.932
1.752	3.419	1.667	0.953
1.648	2.719	1.071	0.650
1.497	2.852	1.355	0.905
1.507	3.022	1.515	1.005
1.411	2.816	1.405	0.995
1.425	2.799	1.374	0.964
1.453	2.796	1.343	0.923
			0.916

TABLE VI

WEIGHT OF WATER ADSORBED BY DRIED STARCH GEL IN GRAMS AT TEMPERATURE ABOUT 35° C.

Original starch gel taken	After 24 hours in water	Gain	Water adsorbed per gram starch
1.716	3.680	1.964	1.144
1.531	3.300	1.769	1.155
1.825	3.930	2.102	1.149
1.580	3.306	1.726	1.092
1.564	3.230	1.666	1.065
2.064	4.296	2.232	1.081
1.759	3.843	2.084	1.184
2.001	4.169	2.168	1.081
1.161	2.605	1.444	1.243
1.216	2.686	1.470	1.208
			1.140

TABLE VII

WEIGHT OF WATER ADSORBED BY DRIED STARCH GEL IN GRAMS AT TEMPERATURE ABOUT 50° C.

Original starch gel taken	After 24 hours in water	Gain	Water adsorbed per gram starch
0.519	1.791	1.272	2.450
0.830	2.838	2.008	2.407
0.760	2.535	1.765	2.322
0.895	3.079	2.174	2.429
0.812	2.782	1.970	2.426
0.766	2.655	1.889	2.466
0.726	2.506	1.780	2.451
0.898	3.023	2.125	2.366
0.845	2.935	2.090	2.473
0.618	2.147	1.529	2.474
			2.426

TABLE VIII

WEIGHT OF WATER ADSORBED BY DRIED STARCH GEL IN GRAMS AT TEMPERATURE ABOUT 60° C.

Original starch gel taken	After 24 hours in water	Gain	Water adsorbed per gram starch
0.796	2.983	2.187	2.747
0.350	1.306	0.956	2.731
0.804	2.981	2.177	2.707
0.468	1.744	1.276	2.726
0.592	2.145	1.553	2.623
0.489	1.905	1.416	2.895
0.770	2.860	2.090	2.714
0.670	2.664	1.994	2.976
0.752	3.011	2.259	3.003
0.740	2.921	2.181	2.947
			2.807

TABLE IX

WEIGHT OF WATER ADSORBED BY DRIED STARCH GEL IN GRAMS AT TEMPERATURE ABOUT 70° C.

Original starch gel taken	After 24 hours in water	Gain	Water adsorbed per gram starch
0.468	1.944	1.476	3.154
0.402	1.610	1.208	3.004
0.644	2.622	1.978	3.071
0.513	2.105	1.692	3.298
0.637	2.613	1.976	3.102
0.433	1.866	1.433	3.307
0.809	3.377	2.568	3.171
0.800	3.368	2.568	3.210
0.921	3.785	2.864	3.109
0.595	2.446	1.851	3.107
			3.153

TABLE X

WEIGHT OF WATER ADSORBED BY DRIED STARCH GEL IN GRAMS AT TEMPERATURE ABOUT 80° C.

Original starch gel taken	After 24 hours in water	Gain	Water adsorbed per gram starch
0.656	2.693	2.037	3.105
0.519	2.246	1.727	3.327
0.674	3.056	2.382	3.534
0.968	4.375	3.407	3.519
0.729	3.146	2.417	3.315
0.700	3.058	2.358	3.368
0.600	2.810	2.210	3.683
0.975	4.232	3.257	3.340
0.598	2.748	2.150	3.595
0.679	3.045	2.366	3.484
			3.427

TABLE XI

WEIGHT OF WATER ADSORBED BY DRIED STARCH GEL IN GRAMS AT TEMPERATURE ABOUT 90° C.

Original starch gel taken	After 24 hours in water	Gain	Water adsorbed per gram starch
0.968	4.417	3.449	3.563
0.954	4.462	3.508	3.677
0.588	2.677	2.089	3.552
0.636	2.995	2.359	3.709
0.798	3.849	3.051	3.823
0.736	3.011	2.275	3.091
0.819	3.986	3.167	3.866
0.836	4.076	3.240	3.875
0.752	3.810	3.058	4.066
0.664	3.262	2.598	3.912
			3.713